This difference between the Debye temperatures, $\Theta_D$ and $\Theta_M$, has been pointed out by Zener and Bilinsky[4] who show that $\Theta_M$ is always the larger by a few percent.

## APPLICATION OF EQUATIONS

For crystals with an anisotropic factor of less than 2, Reuss' equations for $\bar{s}_{ik}$ give Debye temperatures differing by less than 1% from the values obtained from the elaborate procedure recommended by Sutton.[5] When the anisotropic factor is greater than 2, the average values of $\bar{s}_{11}$ and $\bar{s}_{44}$ given by both Voigt's and Reuss' equations give better agreement than either alone, the Debye temperatures, at least for the metals where $c_{11}-c_{12}<2c_{44}$, lying between the values calculated by Sutton's expressions and by Hopf and Lechner's method as modified by Keesom and Pearlman.[6]

Table I shows values of the Debye temperature, $\Theta_D$, for a number of crystals of varying anisotropic factor, $F$, the Debye temperatures having been calculated from the average moduli of compliance as given by both Voigt's and Reuss' equations. The corresponding values obtained from Sutton's method are given in the final column headed $\Theta_D(S)$.

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[4] C. Zener and S. Bilinsky, Phys. Rev. **50**, 101 (1936).

[5] P. M. Sutton, Phys. Rev. **99**, 1826 (1955).

[6] N. Pearlman and P. H. Keesom, Phys. Rev. **88**, 398 (1952).

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# Long-Time Components in the Emission of Luminescent Materials*

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The decay of light emission in the time range from 150 microseconds to 20 milliseconds, caused by excitation by single high-energy electrons and alpha particles at room temperature, was studied for several different types of phosphors. The zinc cadmium sulfides investigated were found to exhibit emission under alpha particle excitation longer than can be accounted for by the bimolecular decay theory, indicating that traps are of importance even with this kind of excitation. Several alkali halides also emit a considerable part of their total light in this interval when excited by alpha particles. Of the organic phosphors studied, only diphenylacetelene showed measurable emission in this time range, and only when excited by alpha particles. A phosphor with a very large number of traps (Standard 7) had practically no emission in the time range investigated.

## 1. INTRODUCTION

THE influence of traps on the light emission of various phosphors from 2.5 milliseconds after the beginning of excitation to hours was discussed in a previous publication.[1] The shapes of the rise of fluorescence curves presented there were due to the cooperative effects of the many electrons excited by high-energy radiation. Additional information on the light emission will be given here, in particular, on the amount of light emitted up to various times in the range from 150 microseconds to 20 milliseconds due to excitation by single high-energy electrons and alpha particles at room temperature. There have been many investigations[2] of long-time emission induced by high-energy particles and quanta, cathode rays, and light. It is difficult to correlate the results of the latter two with the present results where high-energy particles were used to excite the phosphors, because such particles produce an appreciable excitation in a very short interval of time and within a relatively small area.[1]

## 2. EXPERIMENTAL PROCEDURE

### (a) Excitation

Since the intensity of the light emission due to a single fast electron is low, particularly several hundred microseconds after excitation, excitation was furnished by a burst of high-energy electrons, about 1500 in number, in a time interval of about 150 microseconds (or about 100 alpha particles in the same interval). The observed emission was equivalent to that of the sum of 1500 (or 100) single particles, since other measurements[1] showed that with these numbers there is little overlap of the areas excited by different particles when the sample is de-excited prior to excitation. This excitation by a burst instead of by a single particle introduces an uncertainty of ±75 microseconds in the emission time.

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* This work was supported by the Signal Corps Engineering Laboratories, Evans Signal Laboratory, Belmar, New Jersey.

[1] H. Kallmann and G. M. Spruch, Phys. Rev. **103**, 94 (1956).

[2] H. W. Leverenz, *An Introduction to Luminescence of Solids* (John Wiley & Sons, Inc., New York, 1950), p. 263 ff; see P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949) for an extensive bibliography. Some of the more recent papers are: J. Bonanomi and J. Rossel, Helv. Phys. Acta **25**, 725 (1952); I. Broser and C. Reuber, Z. Naturforsch. **9a**, 689 (1954); J. R. Cook and K. A. Mahmoud, Proc. Phys. Soc. (London) **B67**, 817 (1954); C. R. Emigh and L. R. Megill, Phys. Rev. **93**, 1190 (1954); Williams, Usiskin, and Dekker, Phys. Rev. **92**, 1398 (1953); F. B. Harrison, Nucleonics **12**, 24 (1954); J. A. Jackson and F. B. Harrison, Phys. Rev. **89**, 322 (1953).

A double rotating wheel shutter provided approximately three bursts of high-energy particles per second, each of about 150 microseconds duration. It consisted of a fast wheel rotating at a speed of about 2500 rpm, with two rectangular openings on its circumference 0.5 cm by 1 cm, 180° apart, and a slow wheel of the same diameter, concentric with the first, rotating at a speed of about 180 rpm, and with a rectangular opening 0.65 cm by 1 cm on its circumference. The speed of the second wheel could be varied by means of gears and a friction drive. The fast wheel determined the duration of the bursts from a source of high-energy particles placed behind the wheels, while the slow wheel determined the frequency of the bursts.

### (b) Materials Investigated

Several different types of phosphors were selected for study in order to learn what differences might exist in their behavior. Where it was necessary, the phosphors were de-excited before each measurement. This was described previously,[1] as were their chemical compositions. The zinc cadmium sulfides, strontium sulfide, and the uranyl salts were in powder form, deposited in a thin layer onto a Lucite backing. Several alkali halides and the organic phosphors anthracene, stilbene, naphthalene, and diphenylacetylene were studied as crystals. An anthracene flake and a stilbene melt were also investigated.

### (c) Detection

The light was detected by a 1P21 photomultiplier housed in a light-tight brass chamber which also contained the phosphor. The high-energy particles entered the chamber through a thin aluminum window of the same dimensions as the opening on the fast wheel. The photomultiplier output was connected to an oscilloscope via an electrometer tube circuit whose time constant could be varied, and which was generally much longer than the duration of the burst. The oscilloscope traces were photographed.

The trace from a fast phosphor such as anthracene (decay time$\sim 10^{-8}$ sec) showed an initial rise corresponding to the emission during excitation, followed by a decay of the voltage due entirely to the circuit. The maximum of this trace occurred at the time excitation terminated, $t_0$, even for the longest circuit time constant. A phosphor with long-time emission produced a trace whose initial rise was similar to that of the fast phosphor, but the rise continued after excitation had terminated, so that the maximum of the pulse occurred at $t_m > t_0$. As the time constant of the circuit was made shorter, the maximum on the trace appeared at shorter times as well as being smaller in height, because for the shorter time constants of the circuit, charge leaked off the condensers during the time that charge from the photomultiplier was still arriving.

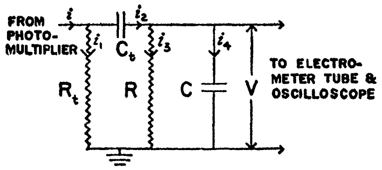

FIG. 1. Schematic diagram of photomultiplier output circuit.

### (d) Method of Determining the Light Emission as a Function of Time

The light emission was obtained as a function of time by measuring the maximum amplitude of the oscilloscope trace and the time at which it occurred. If the shape of the light decay curve is known to be exponential, its time constant can be determined from the heights of the maxima of the voltage pulses observed for different circuit time constants.[3] If the shape of the decay curve is not known, it is also necessary to observe the time at which the voltage maxima occur as a function of the time constant of the circuit.

With the circuit as shown in Fig. 1, one has

$$V = i_3 R = \frac{1}{C}\int_0^t i_4(t')dt', \qquad (1)$$

and

$$-i_1 R_t + \frac{1}{C_t}\int_0^t i_2(t')dt' + i_3 R = 0. \qquad (2)$$

It is desirable to express the photomultiplier current $i$ in terms of $i_3 R = V$ since this is what is measured. At $t_m$, the time at which the voltage pulse reaches its maximum value, $dV/dt = 0$. Straightforward differentiation and combination of the above equations with the current relations leads to

$$i(t_m) = V_m\left(\frac{1}{R_t} + \frac{1}{R} + \frac{C}{R_t C_t}\right) + \frac{1}{R_t C_t}\int_0^{t_m} i_3(t)dt. \qquad (3)$$

As long as $t_m/R_t C_t$ is very much smaller than unity, the integral term can be neglected in comparison to the first term in (3). Since this was generally the case, to a sufficient degree of accuracy one remains with

$$i(t_m) \simeq V_m(1/R_t + 1/R + C/R_t C_t). \qquad (4)$$

Equation (4) gives $i$ at the time $t_m$. The quantities $t_m$ and $V_m$ are measured. By varying $R$ ($R_t$ and $R$ were always equal), $i$ is obtained as a function of $t$.

Instead of using the maximum voltage and the time when it occurred to determine $i$, one could have measured $i$ directly, by employing a circuit with a short time constant.[4] Then the current would have consisted of single small pulses close to the base line of the oscilloscope. In the present method, because of the long time constant of the circuit, the measured voltage was always far above the base line. In addition, because the inte-

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[3] Broser, Kallmann, and Reuber, Z. Naturforsch. **5a**, 79 (1950); Bittman, Furst, and Kallmann, Phys. Rev. **87**, 83 (1952).

[4] J. Bonanomi and J. Rossel, Helv. Phys. Acta **25**, 725 (1952).

TABLE I. Light emission in various time intervals.

| Substance[a] | Excitation | $t_0$[b] μsec | $t_{m1}$[c] μsec | Emission up to various times $t$ (in microseconds) following termination of excitation in percent of emission during excitation[d] | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $t \to 250$ | 400 | 500 | 800 | 1000 | 1250 | 2000 | 2500 | 5000 | 8000 | 10 000 | 15 000 | 20 000 |
| KBr(Tl) | β | 140 | 700 | ··· | ··· | ··· | 113 | ··· | ··· | 208 | ··· | 277 | 300 | 308 | 318 | 321 |
| | α | 170 | 290 | ··· | 39 | ··· | 74 | ··· | ··· | 110 | ··· | 119 | ··· | ··· | ··· | 119 |
| NaCl (AgCl 5%) | β | 170 | 170 | 13 | ··· | 39 | ··· | ··· | 73 | ··· | 94 | 111 | 117 | 120 | 122 | 122 |
| | α | 180 | 240 | 12 | ··· | 30 | ··· | ··· | 51 | ··· | 66 | 76 | 78 | 79 | ··· | 79 |
| CsBr(Tl) | β | 140 | 220 | ··· | 36 | ··· | 59 | ··· | ··· | 91 | ··· | ··· | 115 | ··· | 118 | 118 |
| | α | 180 | 180 | ··· | 15 | ··· | 16 | ··· | ··· | ··· | ··· | ··· | ··· | ··· | ··· | 16 |
| ZnS *D* | β | 130 | 240 | 21 | ··· | 40 | ··· | ··· | 61 | ··· | 74 | 84 | ··· | 90 | 91 | 92 |
| | α | 160 | 160 | 5 | ··· | 10 | ··· | ··· | 14 | ··· | 16 | 16.5 | ··· | ··· | ··· | 16.5 |
| ZnS *LG* | β | 220 | 220 | ··· | 16 | ··· | ··· | 37 | ··· | 50 | ··· | 64 | 67 | 68 | ··· | 68 |
| | α | 180 | 180 | ··· | 14 | ··· | ··· | 30 | ··· | 38 | ··· | 44 | 45 | ··· | ··· | 45 |
| ZnCdS *K* | β | 190 | 190 | 4 | ··· | 10 | ··· | 13 | ··· | 14 | ··· | ··· | ··· | ··· | ··· | 14 |
| | α | 180 | 180 | 9 | ··· | 19 | ··· | 24 | ··· | 26 | ··· | ··· | ··· | ··· | ··· | 26 |
| ZnCdS *L* | α | 130 | 130 | 16 | ··· | 31 | ··· | 39 | ··· | 42 | ··· | 43 | ··· | ··· | 44 | 44 |
| Uranyl acetate | β | 180 | 290 | ··· | ··· | 39 | ··· | 47 | ··· | ··· | ··· | ··· | ··· | ··· | ··· | 47 |
| Potassium uranyl sulfate | β | 170 | 580 | ··· | ··· | ··· | ··· | 110 | ··· | 126 | 127 | ··· | ··· | ··· | ··· | 127 |
| | α | 170 | 380 | ··· | 40 | 54 | ··· | 83 | ··· | 90 | ··· | ··· | ··· | ··· | ··· | 90 |
| Standard 7 | β | 200 | 200 | ··· | ··· | 5 | ··· | ··· | ··· | ··· | ··· | ··· | ··· | ··· | ··· | 5 |
| | α | 110 | 110 | 4 | ··· | ··· | ··· | ··· | ··· | ··· | ··· | ··· | ··· | ··· | ··· | 4 |
| Diphenyl-acetylene | α | 180 | 180 | 6 | ··· | 9 | ··· | 11 | ··· | 12.5 | 12.7 | 12.8 | ··· | ··· | ··· | 12.8 |

[a] These phosphors are characterized more completely in reference 1.
[b] $t_0$ denotes the termination of excitation in microseconds.
[c] $t_{m1}$ is the time of occurrence in microseconds of the maximum voltage with the shortest circuit time constant.
[d] The accuracy of the absolute values in the table is not as great as the number of significant figures would imply. The differences between successive values for a single substance are meaningful, however.

grated intensity was measured, the quantities involved were much larger than if $i$ had been measured directly at different times.

The amount of light emitted in the various time intervals after the termination of excitation at $t_0$ compared to that emitted up to $t_0$ is obtained as follows. The amount of light emitted up to $t_0$ is proportional to

$$\int_0^{t_0} i(t)dt = \int_0^{t_0} V\left(\frac{1}{R_t}+\frac{1}{R}\right)dt + 2\tau\frac{V_{t_0}}{R} \approx 2\tau\frac{V_{t_0}}{R} \quad \text{when} \quad t_0 \ll \tau, \qquad (5)$$

where $\tau = RC/2$, and that emitted from $t_0$ to a time $t$ is proportional to $\int_{t_0}^{t} i(t')dt'$, where $i(t')$ is obtained from the various values of $V_m$ and $t_m$ using Eq. (4).

### (e) Determination of the Duration of Excitation

The time at which excitation ceased, $t_0$, was determined from the speed of the fast wheel while the slow wheel remained fixed with its opening between the source and phosphor. The pulses generated by the openings on the fast wheel were made to form a stationary pattern on the oscilloscope screen, the sweep speed adjustment giving the time for a given number of revolutions. A speed measurement was taken at the beginning and end of each run, since the speed of the wheel did not remain completely constant.

With a fast phosphor the value of $t_0$ obtained in the manner described above could be checked, for in that case $t_0$ equalled $t_{m1}$, the time of occurrence of the maximum voltage with the shortest circuit time constant, and $t_{m1}$ was easily obtained from the photographic trace. The average difference between the values of $t_0$ determined from the two methods was 11%, the maximum difference 23%.

The determination of $t_0$ constituted the greatest source of error in the determination of the amount of light emitted in the different time intervals compared to that emitted up to $t_0$. The error is greatest in the first interval after $t_0$, however, for an error in the determination of $t_0$ affects both the size of the interval up to $t_0$ and the size of the first interval after $t_0$, and thus the error is compounded.

### (f) Spread of the Experimental Points

For the lower circuit resistances ($10^5$ and $10^6$ ohms) the camera was left open for three minutes, permitting about 500 pulses to be photographed on a single frame. The height and position in time of the maximum was measured, giving a single point for each resistance. With the higher resistances noise sometimes caused the base line to fluctuate. In those cases the oscilloscope screen was observed by eye and only the largest pulses were photographed, each on a single frame, about fifteen during a period of about three minutes, for each resistance. The lowest point on the curve, that corresponding to the $10^8$-ohm resistance, was the most difficult to obtain. The maximum was broadest for that resistance, introducing uncertainty in the time when the maximum occurred. Roughly 1500 electrons impinge upon the phosphor and impart $5\times10^7$ ev to it in a single burst (assuming a ZnS sample 25 mg/cm² thick). In the first few hundred microseconds only about 1% of this energy is emitted as light,[1] and only about 10% of this latter quantity is emitted in the interval from 2 to 5 milliseconds. Thus $10^4$ photons are emitted during this period, only $10^3$ of which reach the photomultiplier cathode. For a photoelectric conversion efficiency of 10%, only 100 primary electrons are produced. With a lower efficiency, corresponding to phosphor emission in the region of the spectrum where the photomultiplier is less sensitive, even fewer electrons are produced. Thus large fluctuations in the time when the maximum occurs are to be expected for the lowest point on the decay curve.

## 3. RESULTS

### (a) General Remarks

The results are given in Table I. The values given represent the light emitted between $t_0$ and the times indicated in percent of the light emitted up to $t_0$. For almost all the zinc cadmium sulfides studied, the decay of phosphorescence under alpha-particle excitation was faster than under electron excitation, as was expected, but was slower than would be predicted by the bimolecular decay process usually assumed for these phosphors. That is, the amount of light emitted within one millisecond after the termination of excitation is an astonishingly large fraction of the emission during excitation, and is not very much smaller than the corresponding quantity with electron excitation. If one assumes that most of the electrons excited by alpha particles are in the conduction band and not in traps, one would expect a faster decrease in light emission. The total amount of light emitted up to the time $t$, $\int_0^t Idt'$ should decay as $\{n_H-[\beta^*(1/\beta^* n_H+t)]^{-1}\}$ according to a bimolecular decay theory. For reasonable values of $\beta^*$,[5] the radiation recombination coefficient, and $n_H$, the number of activators per unit volume occupied by positive charges, the light emission should be negligible after several microseconds, if most of the electrons are in the conduction band. That this is not the case, and the fact that the ratio of the light emitted from $t_0$ up to one or two milliseconds to that emitted up to $t_0$ is not too much smaller than for electrons, indicates that for alpha-particle excitation as well as for electron excitation traps are of importance, and that there is a large number of shallow traps from which electrons are released after a rather short time. These extend the emission excited by alpha particles. It may be noted that in the interval from termination of excitation to milliseconds the actual emission is much larger for alpha particles than for electrons for the same amount of absorbed energy, though the emission in this region relative to that during excitation is smaller for alpha particles. The amount of light induced in the first 100 microseconds by high-energy electrons is only ten percent or less of the total light emitted, whereas the light induced in this time by alpha particles is fifty percent or more of the total.[1] The results of Broser and Reuber[5] confirm the bimolecular decay theory up to about one microsecond for ZnCdS phosphors. The results of the present investigation show that there is additional emission which extends up to milliseconds. Though the intensity of the emission is weak, the total emission in this range is comparable to that in the first 100 microseconds, but it is different for different phosphors of this type. Observation of the light emitted by one alpha particle has further indicated that the emission in the first microsecond is comparable to or less than that in the next 100 microseconds.

Another feature which emerged from the investigation was that only one of the organic phosphors, diphenylacetylene, exhibited measurable emission after the termination of excitation. Thus no emission curves could be obtained for anthracene, naphthalene, and stilbene, in any form, whether excited by alpha particles or by electrons. For these substances practically all the light had been emitted by the time the opening on the wheel had passed,[6] and the maximum voltage always occurred at the time excitation terminated, $t_0$, with the maximum voltage the same for the $10^6$, $10^7$, and $10^8$ ohm resistances. Only for the $10^5$-ohm resistance was the maximum voltage smaller, for then the circuit time constant was of the same order as $t_0$, and some charge leaked off the condenser during excitation.

### (b) Results for Individual Phosphors

For diphenylacetylene the situation is quite different from that of the other organic phosphors. Here, while the behavior under electron excitation is the same as for the other organic phosphors, under alpha-particle excitation there is a long-time emission which is decidedly outside the limits of experimental error. Almost ten percent of the light emitted during excitation is emitted in the 300 microseconds following the termination of excitation, with a few more percent being emitted in the next 1000 microseconds. One cannot state at this point to what process this emission must be attributed.

Most of the alkali halides investigated exhibited more long-time emission than the zinc cadmium sulfides. Figure 2 shows decay curves for KBr(Tl). These give evidence of a large number of relatively shallow traps. Even for alpha-particle excitation more than one hundred percent of the light emitted during excitation is emitted in the 2000 microseconds subsequent to excitation. The maximum on the voltage pulse with the smallest circuit resistance occurred well beyond termination of excitation, at 290 microseconds for alpha-particle excitation, and at 700 microseconds for electron excitation. NaCl(AgCl 5%) and CsBr(Tl) exhibited considerable emission in the time range studied for both types of excitation. CsI, however, both unactivated and thallium-activated, showed no measurable

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[5] I. Broser and C. Reuber, Z. Naturforsch. **9a**, 689 (1954), give $\beta^* n_0 \simeq 3\times 10^6$; See also H. Kallmann and B. Kramer, Phys. Rev. **87**, 91 (1952).

[6] The long-time emission reported by Jackson and Harrison,[2] and by Bittman, Furst, and Kallmann[3] extended only up to microseconds, and was very low in intensity.

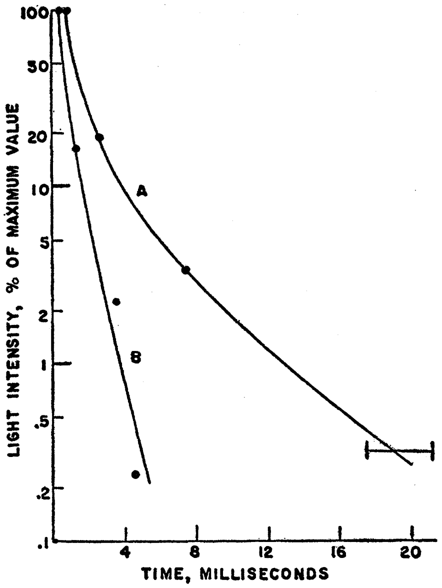

FIG. 2. Decay of light emission in KBr(Tl); curve *A*: after high-energy electron excitation; curve *B*: after alpha-particle excitation.

emission after excitation. This was also the case with $CaWO_4$.

For ZnCdS phosphors excited by alpha particles, the maximum voltage for the smallest time constant of the circuit always coincided with the termination of excitation; with electron excitation it occurred after the termination of excitation only for ZnS *D*. For this phosphor the rise of fluorescence curve[1] exhibited a very sharp increase after the onset of excitation, indicating the presence of electrons trapped for short times. Thus the delayed position of the maximum is consistent with the measurements on the rise of fluorescence, but it is surprising that there is not more long-time emission under alpha-particle excitation.

The light decay curves for the uranyl salts under both electron and alpha-particle excitation could be approximated by single exponentials. For uranyl acetate, though electron excitation terminated at 180 microseconds, the maximum on the pulse did not appear until 290 microseconds, indicating considerable emission during this period. Almost forty percent of the light emitted during excitation is emitted in the 300 microseconds following excitation. By 1000 microseconds after excitation the intensity is down to one percent of the maximum. Potassium uranyl sulfate exhibited longer emission, measurable up to 2500 microseconds. There was no evidence of traps. We assume that the observed long-time emission is intrinsic to the base material. The fact that there was less long-time emission for alpha particle than for electron excitation may be the result of the strong quenching which occurs in the material as a consequence of the high density of excitation produced by alpha particles (the light efficiency is much smaller for alpha particles than for electrons).

The decay for the Standard 7 phosphor is almost instantaneous. One can state that for alpha-particle excitation the intensity drops to less than one percent of maximum within 100 microseconds after excitation. Yet there was evidence of some long-time emission in that the voltage maximum for the longest circuit time constant fell at about 2800 microseconds under alpha-particle excitation. The decay with electron excitation was slightly more noticeable. Within 250 microseconds after the termination of excitation only about five percent of the light emitted during excitation is emitted. Since the rise of fluorescence curve[1] for Standard 7 indicated that this substance possesses a tremendous number of traps, and yet the decay curve has only a very weak tail, two conclusions can be drawn: the number of traps from which electrons are emitted after a short time must be relatively small, and the mechanism for light emission in this substance must be quite different from that of the zinc cadmium sulfides. In the alkaline earth phosphors it is most likely the excitation energy, rather than the separate positive and negative charges, which either encounters a trap or is emitted as light. If these two processes occur with equal probability, then half of the excitation energy is used for light emission and half for trapping, which would account for the fact that the intensity at the onset of electron excitation is roughly half of the stationary intensity.[1] A somewhat analogous situation seems to hold for the organic crystals. Photoconductivity measurements have indicated that in the organic phosphors there are as many traps as in the zinc cadmium sulfides, yet the probability of trapping is negligibly small compared to that of light emission.